GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF RESEARCH ADMINISTRATION

Date: 29 March 1966

RESEARCH PROJECT INITIATION

Project Title: Mass Spectrometric Study of Mobility, Diffusion, and Reactions of Ions in Gases

Project No.: B-2022

Project Director: Drs. David W. Martin and Earl W. McDaniel

Sponsor: Air Force Office of Scientific Research

Agreement Period: From 1 April 1966 until 31 March 1968

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AFOSR (SRKA)
Washington, D. C. 20333

Reports Required

Scientific - whenever results of unusual interest occur.

Final - At expiration of grant.

Assigned to: School of Physics

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RA-3 (4/65)

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RESEARCH PROJECT TERMINATION

Date: December 2, 1970

Project Title: Mass Spectrometric Study of Mobility, Diffusion, and Reactions of Ions in Gases

Project No: B-2022

Principal Investigator: Drs. D. W. Martin and Earl W. McDaniel

Sponsor: Air Force Office of Scientific Research

Effective Termination Date: December 1, 1970

Clearance of Accounting Charges: All acceptable charges have cleared.

Final Technical Report sent August 18, 1970.

Final Fiscal Report sent November 30, 1970.

Final Report of Inventions and Subcontracts sent September 15, 1970.

Title to all equipment purchased vests in the grantee. (Items specified by Attachment 1 of the grant).

This project is continued by B-2036.

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INTERIM SCIENTIFIC REPORT

PROJECT B-2022

MASS SPECTROMETRIC STUDY OF MOBILITY, DIFFUSION, AND REACTIONS OF IONS IN GASES

E. W. MC DANIEL
D. W. MARTIN

AFOSR Grant No. AF-AFOSR - 1118-66

Project-Task No. 9767-02

1 April, 1966 to 31 March, 1968

Issued April, 1968

Research sponsored by the Air Force Office of Scientific Research,
Office of Aerospace Research, United States Air Force

School of Physics
Georgia Institute of Technology
Atlanta, Georgia

I. RESEARCH PERFORMED

During the contract period immediately preceding the grant period covered by this report, a new drift tube mass spectrometer of ultra-high-vacuum construction and unique capabilities was designed and built. This apparatus is described in detail in references 4 and 6 in Section II on Publications. Research with this new apparatus was commenced at about the time that the present grant period started.

Since detailed descriptions of the apparatus have already been submitted, only a brief description will be given here. The experimental facility consists of a large ultra-high-vacuum enclosure containing a drift tube and ion-sampling apparatus, plus associated circuitry. The gas to be studied is admitted to the drift tube through a servo-controlled leak, and the sample gas continuously flows from the tube through an exit aperture on the axis at the bottom of the tube. The pressure in the drift tube is held constant during operation at some desired value in the range 0.02 to 1.0 Torr. A pulsed electron-impact ion source is used to create repetitive, short bursts of primary ions at a selected source position on the drift tube axis. Each burst of ions moves downward out of the source and migrates down the axis of the drift tube under the influence of a weak uniform electric field produced by electrodes inside the tube. When the ions reach the bottom of the drift tube, they are swept out through the exit aperture, and the core of the emerging jet of ions and gas molecules is cut out by a conical skimmer and allowed to pass into an rf quadrupole mass spectrometer. Ions of a selected charge-to-mass ratio traverse the length of the spectrometer, all other ions being rejected in the mass selection process. The selected ions are then detected individually by a nude electron multiplier operated as a pulse counter, and the resulting pulses are electronically sorted as to

their arrival time by a 256 channel time-of-flight analyzer. A spectrum of arrival times is built up by superimposing the data from about 10^6 ion bursts for a given source position, and then the procedure is repeated for various other positions of the source along the axis of the drift tube. Following this, the mass spectrometer is tuned successively to other ionic masses, and arrival time spectra are acquired for each type of ion present in the drift tube.

If a given type of primary ion travels all the way from the ion source to the exit aperture without undergoing chemical reactions with the gas molecules, its arrival time spectrum consists of a Gaussian peak slightly skewed toward later arrival times. By a kinetic theory analysis of the motion of the ions in the drift tube, it can be shown how the position of the arrival time peak is related to the drift velocity, or mobility, of that species and how the width and area of the peak are related to the diffusion coefficient of the ions. Hence, for non-reacting ions, the mobility can be easily determined, and the diffusion coefficient may also be obtained if certain perturbing effects are avoided. For ions which do react with the gas molecules, a more elaborate analysis still permits, in simple cases, the evaluation of the mobility and diffusion coefficient, and furthermore the reaction rates can be determined if the reaction pattern is not too complex.

During 1966 and 1967, the apparatus was used to make the following measurements: (a) the drift velocities of H^+ and H_3^+ ions in H_2 and D^+ and D_3^+ ions in D_2 at room temperature over a range of E/p_o extending from about unity to about 200 volt/cm-Torr. (b) the rate coefficients for the reactions $H^+ + 2H_2 \rightarrow H_3^+ + H_2$ and $D^+ + 2D_2 \rightarrow D_3^+ + D_2$ for ions in thermal equilibrium with the gas at room temperature. (c) the drift velocities of

Li^+, Na^+, and K^+ ions in both H_2 and D_2 at room temperature over the same E/p_o range as covered in (a). The rate coefficients for the reactions in (b) were the first ever obtained for these reactions, and we believe that our values are among the most accurate which have been measured for three-body ion-molecule reactions.

The drift velocities of the alkali ions were measured as a check on possible systematic errors in our experiments. These ions are known not to undergo reactions with hydrogen molecules at room temperature, and their drift velocities have been very accurately measured in other laboratories with drift tubes without mass spectrometer attachments. Hence it was believed that any discrepancies between our new results and the existing data might illuminate certain kinds of systematic errors on our part. However, our data were in excellent agreement with the other results, and so we proceeded with confidence.

At various times during 1967, we made changes in our apparatus to upgrade its performance. These changes included: (a) substitution of a new rf quadrupole mass spectrometer to obtain better stability and higher mass resolution, (b) replacement of the original ion source with a new one equipped with a Tyndall grid to give us better control over the production of ions and narrower ion pulses, (c) substitution of an improved electron multiplier tube which gives us a much higher signal-to-noise ratio in ion detection, (d) installation of internal electrical heating elements around the outside of the drift tube to allow us to bake the apparatus at a higher temperature during pump-down and provide a much lower base vacuum.

During 1967, we also made preliminary measurements of the drift velocities of N^+, N_2^+, N_3^+, and N_4^+ ions in N_2, and in January and February of 1968,

these measurements were completed. We now have final drift velocity data on N^+ and N_2^+ ions in N_2 up to an E/p_o of about 250 volt/cm-Torr and on N_3^+ and N_4^+ ions in N_2 up to an E/p_o of about 15 volt/cm-Torr. (Breakup of the N_3^+ and N_4^+ ions in collisions with gas molecules prevented reliable measurements from being made at higher E/p_o.) We have also measured the drift velocity of K^+ ions in N_2 up to an E/p_o of about 120 volt/cm-Torr.

Our data demonstrated that N_3^+ and N_4^+ ions are formed in N_2 by the following reactions:

$$N^+ + 2N_2 \rightarrow N_3^+ + N_2$$

$$N_2^+ + 2N_2 \rightarrow N_4^+ + N_2 \ .$$

We have obtained the rate coefficients for both of these reactions for ions in thermal equilibrium with the gas at a temperature of 300°K. In addition, the rate coefficient for the first reaction was measured at E/p_o ranging up to 100 volt/cm-Torr.

Finally, data have been obtained to permit the evaluation of the longitudinal and transverse diffusion coefficients for N^+, N_2^+, N_3^+, N_4^+, and K^+ ions in N_2. These data are being analyzed, and the final results are expected by June 1, 1968.

All of the measurements on the various ions in nitrogen will be described in detail in a report to be prepared during the summer of 1968.

II. PUBLICATIONS

1. D. L. Albritton, T. M. Miller, J. T. Moseley, D. W. Martin, and E. W. McDaniel, "Mobilities of H^+ and H_3^+ Ions in Hydrogen Gas", Gaseous Electronics Conference, Atlanta, Oct., 1966.

2. T. M. Miller, J. T. Moseley, D. W. Martin, and E. W. McDaniel, "Measurement of the Thermal Reaction Rate Coefficient for $H^+ + 2H_2 \rightarrow H_3^+ + H_2$", Fifth International Conference on the Physics of Electronic and Atomic Collisions, Leningrad, July, 1967.

3. D. L. Albritton, T. M. Miller, J. T. Moseley, D. W. Martin, and E. W. McDaniel, "Mobilities of Mass-Identified H^+ and H_3^+ Ions in Hydrogen", Eighth International Conference on Phenomena in Ionized Gases, Vienna, August, 1967.

4. D. L. Albritton, D. W. Martin, E. W. McDaniel, T. M. Miller, and J. T. Moseley, "Measurement of the Low-Energy Transport Parameters of Mass-Identified Ions in Gases; Mobilities of H_3^+ and H_1^+ Ions in Hydrogen", Georgia Inst. of Technology Technical Report, May 10, 1967. A copy of this report has been sent to AFOSR.

5. T. M. Miller, D. W. Martin, E. W. McDaniel, J. T. Moseley, and R. M. Snuggs, "Measurement of the Low-Energy Transport Parameters of Mass-Identified Ions in Gases; Reactions of H^+ in H_2 and D^+ in D_2 and Mobilities of Hydrogen and Alkali Ions in H_2 and D_2", Georgia Inst. of Technology Technical Report, February, 1968. A copy of this report has been sent to AFOSR.

6. D. L. Albritton, T. M. Miller, D. W. Martin, and E. W. McDaniel, "The Mobilities of Mass-Identified H_3^+ and H^+ Ions in Hydrogen", accepted by Physical Review. A preprint of this paper has been sent to AFOSR.

7. T. M. Miller, J. T. Moseley, D. W. Martin, and E. W. McDaniel, "Reactions of H^+ in H_2 and D^+ in D_2; Mobilities of Hydrogen and Alkali Ions in H_2 and D_2 Gases", submitted to Physical Review. A preprint of this paper has been sent to AFOSR.

III. PERSONNEL

A. Permanent Staff Members

1. Dr. E. W. McDaniel, Professor of Physics
2. Dr. D. W. Martin, Professor of Physics

B. Graduate Student Assistants

1. D. L. Albritton
2. T. M. Miller
3. J. T. Moseley
4. R. M. Snuggs

IV. DEGREES EARNED

A. D. L. Albritton - Ph.D. in Physics, Georgia Institute of Technology, June, 1967.

B. T. M. Miller - Ph.D. in Physics, Georgia Institute of Technology, February, 1968.

V. PATENTABLE INVENTIONS

No patentable inventions have been made by any of the personnel engaged in this research.

Respectfully submitted,

Earl W. McDaniel
Co-Project Director

B 2022

AFOSR 70-1994TR

MASS SPECTROMETRIC STUDIES OF MOBILITIES, DIFFUSION, AND REACTIONS OF IONS IN GASES

By

David W. Martin and Earl W. McDaniel

FINAL REPORT

Covering the period

1 April, 1966 to 30 June, 1970

Grant No. AF-AFOSR 1118-66
Project-Task No. 9767-02

Research Sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, United States Air Force

JULY 1970

School of Physics
GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia

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AFOSR 70-1994TR

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Atlanta, Georgia 30332

TABLE OF CONTENTS

ABSTRACT

A previously developed Drift Tube Mass Spectrometer apparatus, for the study of the drift transport in weak fields of low density ion swarms in gases, has been applied to the quantitative measurement of drift velocities and mobilities, of longitudinal and transverse diffusion coefficients, and of the nature, order, and rate coefficients of ion-molecule reactions. Completed studies include, in the gases H_2, D_2, N_2, O_2, and NO, all of the positive (and for O_2 and NO also the negative) ion species found to be formed from the molecules of the gas by electron bombardment, or formed by reactions of such primary ions with the molecules of the gas. The mean ion energies, controlled by the ratio of the electric field strength E to the gas number density N, vary from essentially thermal energy (at room temperature) to as much as several electron-Volts, over the range of E/N of the measurements. A comprehensive though qualitative description is given of the very significant advances that have been made in the capabilities of ion swarm methods to yield new kinds of basic measurements and results of unprecedented accuracy.

I. INTRODUCTION

This report presents a comprehensive descriptive account of the efforts and achievements in the Drift Tube Mass Spectrometer research program at the Georgia Institute of Technology, during the period in which the program was partially supported by the U. S. Air Force Office of Scientific Research through a Grant for Basic Research, No. AF-AFOSR 1118-66. The period covered extends from 1 April, 1966 through 30 June, 1970.

The research work conducted during the tenure of this grant represents a continuation and a fruition of a program which has been developed at the Georgia Institute of Technology by the present authors over a number of years. This program has enjoyed continuous support from its inception by the Office of Scientific Research. The work has centered on the development of an original apparatus concept which we have called a drift tube mass spectrometer, and the use of this device in studies of the transport in weak electric fields of low energy ion swarms in gases. The objectives of such studies are the quantitative measurement of drift velocities and mobilities, diffusion coefficients, and the determination of the nature and rates of reactions occurring between the ions and the molecules of the gas.

II. HISTORICAL AND SCIENTIFIC BACKGROUND

Study of the drift transport of ion swarms in gases was historically one of the earliest means employed to study the interactions of ions with molecules; this general approach continues to be useful for low values of the energy of relative motion (from a few eV down to the thermal energy 3/2 kT), for which single-collision beam experiments encounter very serious difficulties. For the limiting case that the ratio of the applied electric field strength E to the gas number density N is small enough that the drifting ions remain essentially

in thermal equilibrium with the gas, the transport equation for a swarm of non-reacting ions was satisfactorily solved many years ago. Theory and experiment were in agreement, for simple cases, that the mean drift velocity was proportional to the electric field strength. The proportionality constant, called the mobility, was related by the theory to the momentum-transfer collision cross section between the ions and the gas molecules. It was established that in many cases the dominant contribution to this cross section arises classically from the simple point-charge, induced-dipole interaction first proposed by Langevin, expressed by a term in the interaction potential varying with the ion-molecule distance as r^{-4}. In a number of cases, the magnitude of this interaction term deduced from mobility measurements was in good agreement with a value deduced from the macroscopic polarizability of the gas. The variation of the low-field mobility with the gas temperature was related to the variation of the momentum transfer cross section with the relative energy of collision, and yielded information on the magnitude and the form of other terms in the interaction. The energy dependence of the cross section was also known to be manifested in the behavior of the mobility at higher values of E/N, at which the mean energy of the ions increases above the thermal value. The interpretation of the results was much less certain in this case, however, because the theoretical treatment of the ion energy distribution in this situation had not been extensively developed nor well established experimentally.

The early agreement between theory and experiment described here was obtained only for certain simple cases, such as that of an alkali metal ion of low ionization potential in a noble gas of high ionization potential; in such a case there are no possible ion-molecule reactions that are not highly endoergic and hence very improbable at low collision energies. In addition, there was

considerable success in explaining the anomalously small measured mobilities of certain singly charged ions in their own parent gases (where the molecular composition of the molecules and ions differ only in the net charge of the latter) in terms of the additional non-classical scattering mechanism of resonant charge transfer. In many other cases, however, the results were often anomalous and confusing. It became clear eventually that in such cases the molecular composition of the observed ions might be entirely different from what had first been supposed, as the result of chemical reactions between the original ions and the molecules of either the gas itself or of impurities in the gas. It was realized that the latter can be of predominant importance at even very low relative concentrations of the impurity, if the reaction is energetically favored and has a large cross section, because the average number of collisions undergone by each ion in a typical swarm experiment is normally very large. A few of the anomalous cases were eventually cleared up satisfactorily through the introduction of heroic measures to insure extreme levels of gas purity.

However, it soon became clear that the ion composition can also be altered in even very pure gases by reactions of the ions with the molecules of the gas itself. It was to grapple with this situation that the idea of the drift tube mass spectrometer was first conceived by the present authors (and also independently by several others). It has subsequently become well established, in large part through studies with drift tube mass spectrometers, that a rich variety of such reactions is more the rule than the exception, and that there exist many stable ions of previously unexpected molecular compositions that do not exist as neutral molecules. It may be said that the chemistry of singly charged ions has simply proved to be different from, and sometimes rather more complex than, the established chemistry of the corresponding neutral

molecules. The drift tube mass spectrometer has proved to be one of the more powerful approaches available for the elucidation of this chemistry and for the quantitative evaluation of the reaction rates.* Apart from the fundamental interest that attaches to the study of this ion-molecule chemistry, it is of considerable value in a number of situations of practical interest. Included here would be all devices which involve gas discharges, including gas lasers, the chemistry of flames and the subject of combustion generally, aeronomy and the processes of the upper atmosphere, communications problems associated with reentry ionization trails, and so forth. It may be added that the mobility and diffusion coefficient determinations that follow from drift tube studies are also of great practical value in all of these same areas. (See Footnote on page 31).

III. THE DRIFT TUBE MASS SPECTROMETER

A. Concept and Capabilities

The basic concept of the drift tube mass spectrometer can be stated rather simply. (The description given here applies particularly to the apparatus developed in the present program, but also applies generally to most of the systems in use elsewhere that are usually known by the same name.) A pulsed ion source is arranged to introduce, periodically, brief bursts of ions into one end of a cylindrical drift space, which contains the gas of interest at an appreciable pressure (from 0.02 to several Torr in our case). The drift space also contains an electrode arrangement to provide a uniform electric field directed along the tube axis. The collision mean free path of the ions is small compared to the dimensions of the space, so that the swarm drifts in

*Drift tube mass spectrometers are now in use at 13 other laboratories: the University of Pittsburgh, the Bell Telephone Laboratory at Murray Hill, the Bell Telephone Laboratory at Whippany, the University of London, the Australian National University, the Westinghouse Research Laboratory, JILA at the University of Colorado, the Aberdeen Proving Grounds, the Lockheed Missiles and Space Laboratory, Southern Illinois University, Tokyo Metropolitan University, Avco Everett, and the University of Minnesota.

the field direction in a sort of secular equilibrium, with individual ions continually gaining energy from the field and losing energy in scattering collisions. (In the low field or low E/N case, the mean ion energy will exceed the thermal energy of the gas molecules by only a negligible amount.) As the swarm drifts, the ions diffuse both longitudinally (along the field direction) and transversely (at right angles to the field); in addition, the molecular composition of some or all of the ions may be altered one or more times during their transit in a reactive collision with a gas molecule. The detailed time shape of the ion current pulse when it arrives at the far end of the drift space will clearly be influenced by all of these processes.

In a conventional drift tube apparatus, the current of ions arriving at the end of the tube was simply detected in any fashion that permitted the current to be time-analyzed with respect to the time of the source burst. In a drift tube mass spectrometer, on the other hand, a small sample of the arriving ions is first conducted through a differentially pumped orifice into a suitably evacuated region, and thence through a mass-selecting device (an rf quadrupole in our case) to a detector, whose output is then time analyzed as before. In any given run, the mass selector is set to pass ions of only one of the molecular species present in the swarm, so that the analyzed detector output provides a time profile of the swarm of only that one species as it arrives at the sampling orifice. (For a primary ion species formed only in the ion source, in our apparatus, this profile takes the form of an almost Gaussian peak that is slightly skewed toward late arrival times.) A large number of such profiles for all of the species present, for various values of the gas pressure, the electric field strength, and other parameters of the experiment, constitute the raw data which are to be analyzed to evaluate the quantities of interest, i.e., the drift velocities, diffusion coefficients, and reaction rates.

This analysis of the data is a far from trivial matter; much of the basic progress of the present program during the tenure of this grant is in fact centered about developments we have made in this analysis, which will be discussed at some length in Section IV. However, a description in rough outline may be made at this point. One must develop a mathematical description of the swarm density as a function of time and of position in the drift space, from which one can calculate the expected flux of ions arriving at the sampling orifice as a function of time. The quantities of interest will occur as parameters in this calculation, to be evaluated empirically by a process of fitting the calculations to the experimental profiles. Fortunately, each of the quantities of interest is related most closely to some relatively distinct feature of the data, so that we have been able to show that one can largely avoid the necessity of resorting to simultaneous multi-parameter fits. For instance, the drift velocity obviously relates most closely to the overall location of the profile along the time axis (for a primary ion we have demonstrated that it is given quite accurately, with a few restrictions, by the mean arrival time of the whole swarm, i.e., simply by the time location of the centroid of the profile). Similarly, the longitudinal diffusion coefficient D_L is closely related to the time width of the "Gaussian" peak, again for a primary ion. The evaluation of transverse diffusion coefficients (D_T) and reaction rates is not quite so easily described, and discussion of them will be deferred to Section IV of this report.

B. Early Work in this Program

An early version of a drift tube mass spectrometer apparatus of the above general description was developed early in the present program, becoming operational several years prior to the term of the present grant. Separate mobility measurements for two different mass-selected molecular species of hydrogen ions in hydrogen gas, and for four species of nitrogen ions in nitrogen,

were among the very first results of this kind ever published. The accuracy of these early results was poor by present standards, due to various inadequacies of this apparatus and its associated instrumentation, so that the numbers obtained are no longer of more than historical interest. However, this early work established the feasibility of the whole concept, verified for the first time the actual complexity of the reaction schemes to be found in real cases, and indicated at least the possibility that an improved system might be capable of providing quantitative reaction rate determinations. The results also persuaded many of the workers active in this field that some provision for mass selection was almost essential to further progress in drift tube work. Finally, they confirmed, in our view, the potentially great value of one particular unique feature which we had incorporated into this original system for the nitrogen study. This was the provision of a movable ion source, so that the total drift distance could be varied at will over a wide range. This feature, carried over into our present apparatus, continues to the present to be unique among all known apparatus of this type. The flexibility it provides contributes greatly to the range of our capabilities for quantitative measurements.

C. The Present Apparatus

The construction of a completely new and relatively elaborate drift tube mass spectrometer apparatus was begun in this program approximately two years prior to the beginning date of the present grant. Since detailed technical descriptions of this apparatus have been presented in previous reports,[Al,Cl]* it will be described here in only very general terms. All of the latest techniques of ultra high vacuum technology then available were utilized, in order to reduce the interference from competing impurity reactions; the apparatus regularly achieves base vacua in the low 10^{-9} Torr range. The greatest of care

*All references in this report will be to items listed in Section V, Publications.

was given to achieving geometrical accuracy in the configuration of the drift space (the uniformity of the electric field and the positioning of the ion source, sampling orifice, and mass selector). A new type of drift field electrode design was used, for which the field distortions were exactly calculable, and all surfaces that can be "seen" by the low energy ions were made of gold-plated stainless steel. A new open design around the sampling orifice and the largest practicable primary pump were utilized in order to optimize the differential pumping of the orifice and thereby minimize scattering of the ions after their passage through the orifice. The important and unique feature of a movable ion source was retained, utilizing a long metal bellows to transmit mechanical motion from positioning machinery outside the vacuum wall. The drift distance can be varied from 1 to 44 cm at will. The diameter of the drift region is large enough (roughly 7 inches) to be effectively infinite for even the longest drift distance employed. (The use of mass analysis with the concomitant need to conduct an ion sample into an evacuated region has in most cases limited drift tube mass spectrometers to somewhat lower ranges of drift tube gas pressure than was often utilized in conventional drift tubes, and correspondingly larger dimensions of the drift space are therefore indicated. The present apparatus continues to be unique in the large scale of the drift tube dimensions.)

A key feature of both the original and the new versions of this apparatus was the introduction of single-ion detection and of counting techniques, in place of the current measurements common to most earlier drift tube work. The sampling of the arriving ion swarm is just what the term implies, a random sampling of only a minute fraction of all the ions in the swarm. The detected ion "current" is thus orders of magnitude smaller than that in any method that collects a large fraction of the whole swarm. Furthermore, it has been our experience that appreciable space-charged effects in the swarm will distort

and falsify the apparent diffusion coefficients and interfere with reaction rate determinations at much lower swarm densities than we had ever supposed, so that one may not compensate for the inefficient sampling simply by increasing the ion current in the drift tube. The electron multipliers we have used can count single ions effectively at rates even as low as one ion/second, with manageable signal to noise ratios. This order of low-current capability is important to the very feasibility of the drift tube mass spectrometer concept, and is the key to our ability to extend our observations into the regions of very low E/N and/or long drift distances.

The required time analysis of the detector output then takes the form of an electronic sorting of single-ion pulses, according to the time of their occurrence relative to the time of the source burst, into a number of discrete time "channels", and the accumulation of such sorted counts from a large number of identical bursts to achieve adequate counting statistics in the individual channels. There is typically only about one ion detected and sorted from each single burst; with a source burst repetition rate of several hundred/sec, the peak in the profile spread over perhaps 50 time channels, and a statistical requirement of say 1000 counts/channel around the peak, the accumulation of a typical swarm profile takes a few minutes. However, the stability of the system permits one to deviate widely from this typical case, and this fact accounts for our ability to operate over very wide ranges of all of the experimental parameters. For instance, useful time profiles have been obtained, at low E/N, with counting rates so small that the accumulation of a single spectrum required continuous operation for as much as four hours.

The electronic time sorting of detector output pulses is performed by a 256-channel analyzer using a logic that was originally designed for neutron time-of-flight experiments, and all of the pulse handling circuits are of standard nuclear instrumentation types. The mass selector, as mentioned

previously, is a radio frequency (rf) quadrupole instrument. Various types of electron multipliers have been used as the detector, as will be discussed in the next section. The drift tube gas pressure is monitored continuously by a carefully calibrated capacitance manometer, whose output operates a pressure controller having a servo valve in the gas feed line; this system can hold the pressure constant for an indefinite period. A final feature to be mentioned, which has been of no small importance in minimizing unexpected interruptions of the research, is a fairly elaborate network of safety circuits, including an automatic standby power source for the vacuum pumps, which can obviate or at least minimize the effects of unexpected outages of the electric power or cooling water supplies.

The construction of this apparatus in essentially its present form, including the testing, calibration, and evaluation of all of its component systems, was satisfactorily completed at about the close of the period immediately preceding the present grant. There have of course been a succession of modifications since that time to improve the capabilities of the apparatus, as the developing needs of the research demanded or as the possibilities for improvement were manifested in the progress of the research. The more important of these modifications will be mentioned in the next section. Although some of them have been fairly extensive in terms of the effort and expense that were entailed, none have significantly altered the concept of the instrument as described above.

IV. RESEARCH CONDUCTED UNDER THE PRESENT GRANT

It proves to be convenient to organize this discussion around the following three aspects of the work: First is the continuous evolution that has taken place in our analytical techniques for extracting basic numbers from the experimental data, to increase the number of such quantities that can be

obtained, to increase the variety of the situations and/or the ranges of the experimental parameters over which such determinations can be made, or to increase the accuracy and confidence of the determinations; Second is the succession of modifications and improvements that have been made to the apparatus itself, for essentially the same reasons; Finally there is the list of actual cases for which detailed studies have been carried out. All three aspects are of course interrelated, and all were pursued concurrently. It is the first of these aspects that we particularly wish to emphasize in this report, but it happens to be convenient to summarize the other two briefly first.

A. Gases Studied

The gases which have been studied at some length are, in chronological order, H_2, D_2, N_2, O_2, and NO; similar studies of CO have been initiated only recently at the time of this writing. In all cases we have studied all of the positive ions found to be formed from the gas itself by bombardment with electrons of energies of up to around 75 eV, or derived from reactions of such primary ions with the molecules of the gas. In O_2 and NO we have also studied all of the negative ions found to be similarly formed, and in both of these gases we have also measured the mobilities of certain additional ions that are apparently derived from reactions with impurities. In all of the completed cases we have also studied the drift transport in the same gas of at least one species of alkali metal ion. This last item has proved to be quite useful as an overall check on systematic errors, since the mobilities of alkali ions in several of these gases have previously been measured rather accurately by others in higher pressure experiments not involving mass analysis.

In all of the completed cases, the study of each gas was carried to the limits of the state of the art as it existed at the time, and each of the studies has involved some advance in the state of the art in terms of analytical techniques and/or apparatus refinement. The results for the earlier cases H_2, D_2, and N_2 have been fully presented in previous reports and in publications.[A1-5,C1-3] The O_2 results have been fully presented in a report[C4] and in articles that are in final preparation for publication.[B1,2] An article presenting the NO results is now in preparation for publication.[B3] Therefore a detailed presentation of any of these results is not necessary here; we present only a brief catalog of the quantities that have been measured. Every mobility listed here has been measured over a substantial range of the parameter E/N which, in every case, extended to values low enough that the mobility had become constant, giving a reliable value for the limiting or "zero field" mobility. The upper limit of the range varies considerably from case to case, however.

In H_2: Mobilities of H^+, H_3^+, Li^+, Na^+, and K^+:

Transverse diffusion coefficients of H^+ and K^+, over a range of E/N;

Rate of the reaction $H^+ + 2H_2 \rightarrow H_3^+ + H$ in the low E/N limit;

(An evidently loosely bound ion H_5^+ was also observed, but no quantitative measurements were made with respect to it.)

In D_2: Mobilities of D^+, D_3^+, Li^+, Na^+, and K^+;

Transverse diffusion coefficients of D^+ and K^+, over a range of E/N;

Rate of the reaction $D^+ + 2D_2 \rightarrow D_3^+ + D$ in the low E/N limit.

In N_2: Mobilities of N^+, N_2^+, N_3^+, N_4^+, and K^+;

Separate longitudinal and transverse diffusion coefficients of N^+, N_2^+, and K^+ over extended ranges of E/N;

Rate of the reaction $N^+ + 2N_2 \rightarrow N_3^+ + N_2$ over extended range of E/N;

Rate of the reaction $N_2^+ + 2N_2 \rightarrow N_4^+ + N_2$ over extended range of E/N;

(Also observation of the reverse reaction $N_4^+ + N_2 \rightarrow N_2^+ + 2N_2$, with no quantitative determination of the rate.)

In O_2: Mobilities of O_2^+, O^-, O_2^-, and O_3^-; plus relatively qualitative mobilities of O_4^+ and O_4^-; also mobilities of impurity-derived ions CO_3^- and CO_4^-;

Longitudinal diffusion coefficients of O_2^+, O^-, O_2^-, and K^+;

Rate of the reaction $O^- + 2O_2 \rightarrow O_3^- + O_2$ over a range of low values of E/N, by two independent methods;

Rate of the endoergic reaction $O^- + O_2 \rightarrow O_2^- + O$ over a range of values of E/N above 50×10^{-17} volts-cm^2;

Qualitative rates for <u>both</u> reactions of the forward-backward pair $O_2^+ + 2O_2 \rightarrow O_4^+ + O_2$ and $O_4^+ + O_2 \rightarrow O_2^+ + 2O_2$.

In NO: Mobilities of NO^+, $NO^+ \cdot NO$, and K^+;

Longitudinal diffusion coefficients of NO^+ and K^+.

Estimate of the rates of both reactions of the forward-backward pair $NO^+ + 2NO \rightarrow NO^+ \cdot NO + NO$ and $NO^+ \cdot NO + NO \rightarrow NO^+ + 2NO$.

The systematic evolution of our capabilities can be discerned in this chronological list, in the generally increasing scope and detail of the results obtained in the successive studies. There has in fact been a fairly steady acceleration in the rate at which basic information has been produced, even though no systematic decrease is evident in the time required to complete a given study. However, it is also true that not every quantity that is successfully measured in a given case can necessarily be determined in all subsequent cases. Every gas we have studied has presented its own unique difficulties, depending on such things as the details of its reaction pattern,

the relative magnitudes of different terms in the analytical description of the swarm, and so forth. For instance, the rather good separation of transverse diffusion effects from reaction effects in the primary-ion attenuation or "fall-off" method (see following section on analytical techniques) that was possible in nitrogen worked much less well in oxygen, and no transverse diffusion coefficients are listed as having been measured in the latter gas.

B. Apparatus Modifications

The basic design of the ion source has remained unchanged through a succession of modifications to improve its performance or extend its capabilities. A roughly 7-inch diameter front plate filling almost the entire diameter of the drift space provides a plane equipotential surface that defines one end of the uniform drift field. Behind the ion entrance aperture, (a round hole of substantial size in the center of the plate, centered on the drift tube axis) is a large open volume in which the primary ionization of the gas takes place. A repeller electrode at the back side of this space applies a field across the space which is in the same direction as, and normally is of equal intensity to, the drift field itself. A ribbon-shaped beam of electrons, from a filament enclosed in a metal box at one side of the space, and having a slit facing the ionization region, is accelerated through this slit and projected across the space, with the plane of the ribbon perpendicular to the drift tube axis. The electron ribbon is confined by a small, longitudinal magnetic field, so that primary ionization occurs only in an axially thin sheet normal to the tube axis. This sheet moves laterally in the repeller field toward the front plate, where a disc the size of the entrance aperture is cut out and passed into the main drift space.

In the original ion source[A1,C1] used in the early part of the H_2 and D_2 studies, pulsing of the ion source was accomplished solely by pulsing the electron beam admitted to the ionization region, by means of a biased grid in front of the filament. With this arrangement it did not prove practicable to make any determinations of diffusion coefficients. There was excessive axial expansion of the ion sheet within the source volume, due to space charge, unless the initial ion density was kept very low; when this was done, the disc of ions finally admitted to the drift space was of unreasonably low intensity.

The ion entrance aperture has subsequently been increased in size (from about 3/8-inch diameter initially to about 3/4-inch), and fitted with a double-grid shutter or Tyndall gate.[C2] The latter is biased to prevent the passage of any ions except when an appropriate voltage pulse is present on the shutter. Normally the electron beam and the shutter are both pulsed in a suitable sequence, and drift time measurements are taken from the time of the shutter pulse. With a much higher initial ion density in the source, the shutter can admit to the drift space a disc of ions of much greater intensity than before, which is still suitably thin axially and of low enough density not to display any further space charge expansion. The new arrangement also adds another degree of freedom to the parameters of the experiment. When desired, the E/N of the repeller field in the source can be different from that of the main drift field, and the sequence can be set to "age" the ion swarm in the source for an extended time. It is sometimes possible to "drive a reaction to completion" in the ion source, so that a disc of what are really secondary ions can be gated into the drift space just as though they were primary ions.

An independent modification of the ion source consisted of the addition of an alkali-ion source.[C2] These ions are emitted thermionically from a mineral-coated filament, located behind the gas-ionization volume, with an arrangement of grids to gate the alkali ions into the main part of the source and thence into the drift tube. The alkali source does not interfere with the normal operation of the gas ionizer, so that one can switch from gas ions to alkali ions at will, without opening the system. Reasons for wishing to observe the drift of alkali ions in each of the gases studied have been given in the preceding section (IV, A above).

Additional minor modifications to the source were necessitated by specific problems which arose in some of the gases studied. For instance the electron-emitting filament originally used was found to have a very short lifetime in oxygen at higher pressures, and a different type of filament was substituted.[C4] Minor geometrical changes in the arrangement of electrical leads were also required to prevent the short-circuiting of insulating supports by conducting deposits, in this gas. Further details of this sort will not be given here.

To obtain good mobility values for certain of the secondary ions in oxygen, it was necessary to operate the drift tube at higher gas pressures than had been used previously. To accomplish this a smaller sampling orifice was installed as well as a larger main pump, along with certain other mechanical changes.[C4]

The original rf quadrupole was a homemade device of limited resolution. Although it served adequately for the H_2 and D_2 studies, it was inadequate for use with heavier gases, and it was replaced by a commercially purchased instrument of much better resolution.[C2] The latter has served us reasonably well for almost four years, but has also been found to have serious

limitations. The product of resolution and transmission available is inferior to that of more recent instruments, and the reliability of its control circuit leaves something to be desired. We are presently in the process of procurement of a newer and much better instrument to replace it.

A change was made in the type of electron multiplier used as the ion detector when the study of negative ions was begun.[C4] The original discrete-dynode multipliers would have required an excessively high voltage at the anode end, in the electrical configuration for negative ion counting, which would have led to increased noise and degraded signal to noise ratio. This problem was avoided by changing to a channel multiplier fitted with a cone on the input aperture (a so-called "funneltron"). These devices will count ions with high efficiency at substantially lower ion impact energy, and thus do not require as high a potential on the inlet end to accelerate the ions. They have proved to be most satisfactory, and they offer an additional advantage of insensitivity to exposure to air, so this change of detector has been made permanent.

C. Evolution of the Analytical Techniques

It has been explained in an earlier section that the evaluation of drift velocities, diffusion coefficients, and reaction rates from the experimental time profiles of an ion swarm depends upon having a mathematical description of the space-time density of the swarm which contains these quantities as parameters. The description which underlies all of our analytical procedures is an exact, analytic solution of a transport equation for an ion swarm in a uniform electric field with the following idealizations: the form of the transport equation used assumes that ion-ion interactions (space charge effects) are negligible, and that the velocity distribution is independent of position and time; the equation does allow for different values of the diffusion coefficient for space directions parallel and perpendicular to the

electric field, respectively, and for the creation or destruction during the drift period of ions of a given species through reactions. Solutions for various assumptions about the reaction pattern have been obtained for the initial condition that primary ions are introduced instantaneously, at t = 0, distributed as an infinitely thin circular disc of finite diameter oriented perpendicular to the direction of the electric field. All solutions assume such a disc released into a drift space of infinite radial extent and express the subsequent ion density as a continuous function of position and time. From this solution one obtains, in the diffusion approximation, an analytic expression for the flux of ions on a plane, perpendicular to the field, located "downstream" from the source; this function, evaluated at the symmetry axis, represents the current through the sampling orifice as a continuous, analytic function of the time.

A solution of this type for a primary species that has no reaction input (ions of this species are not created from other species by reactions in the drift space) has been compared in detail with actual data for such cases. At very low E/N, it is expected that the longitudinal and transverse diffusion coefficients will be equal to each other at a value that is calculable from the experimental mobility through a simple relation known as the Einstein Equation. This reduction in the number of independent parameters, at low E/N, allows for a much more stringent test of the degree to which the idealized mathematical description of the swarm truly represents the details of the real swarm (or conversely, the degree to which the real experiment truly approximates the mathematical model); one can test not only whether the mathematical description can be fitted closely to the data at all, but in addition whether the empirical values of the diffusion coefficients resulting from such a fit are close to the expected values.

1. Drift Velocity and Mobility.

Early data, taken before the source modification in which the Tyndall gate in the ion entrance aperture was added, did not in general fit the model in detail.[Al,Cl] The peak in the profile was generally much wider than it should be, implying that the longitudinal diffusion coefficient was much larger than its expected value. Furthermore, the implied value of D_L was not repeatable. There were evident space-charge effects in this early data, not only in the width of the peak, but also in the overall time location of the peak, an "end effect" in the apparent mobility that would be inferred from a single observation.

No determinations of diffusion coefficients were therefore taken from any of these early data. It was however shown that reliable values of the mean drift velocity and the mobility could nevertheless be obtained from even such data, with suitable precautions, by the following special technique that does not involve a detailed fit between the data and the model.[Al,Cl] It had been shown from the form of the mathematical model of a primary ion swarm that a first approximation to v_d should be obtained simply by dividing the drift distance z by the mean drift time $\bar{t}$ of the entire profile of the swarm. The expected accuracy of this approximation was first tested numerically as follows. Theoretical swarm profiles were computed for arbitrary assumed values of v_d, of z, and for various values of the diffusion coefficients and of the rate constant of an assumed reaction that depletes the swarm during its drift. These computed profiles were then analyzed, as though they represented real experimental data, according to the simple mean-drift-time rule above. For small values of the reaction rate, the resulting "empirical" value of v_d reproduced the original input value quite accurately (better than 1%) when the values used for the diffusion coefficients were consistent with the assumed v_d through the Einstein Equation; it was further shown that the accuracy of this agreement was insensitive to the values used for the diffusion coefficients over wide limits, or to the value taken

for the reaction rate as long as it was not too large. It was therefore expected that, except for possible end effects, the same procedure applied to real data should also give reliable values for v_d, even if the profile widths were not consistent with the expected values of the diffusion coefficients.

Since the real data did in fact display end effects, the procedure employed was to obtain two experimental profiles for different values of the drift distance z (by utilizing the movable ion source), and to estimate v_d by dividing the difference in drift distances by the difference in mean drift times. As a check, a third profile was always obtained for a third value of z, and checked for consistency with the first two. (Actually, a straight line was always fitted by least squares to the 3 values of $\bar{t}$ vs z, and a number indicating the goodness of fit was calculated, for every "run" consisting of such a set of 3 profiles.)

It was demonstrated that self consistent values of v_d could be obtained in this way from real data, at a given E/N, when the gas pressure was varied widely in order to vary the rate of depleting reactions, or when the initial ion density was varied (by varying the ionizing electron current in the ion source) so as to make appreciable changes in the peak widths and/or in the end effects attributed to space charge.[Al,Cl] Thus it was concluded that good values of v_d could be obtained from even such very imperfect data, for the case of a primary ion, by this simple differencing procedure. The same procedure has been used to evaluate v_d for all subsequent data; it involves only straightforward calculations that are easily programmed to be done by the computer, and by using it there is one less parameter left to be determined in the final "best fit" of the model to the data. The efficacy of this procedure represents the first instance of the great value we attach to our unique feature of a movable ion source.

The same differencing procedure has been applied with considerable success to secondary ions, formed from the primary ions by reactions. Even if it is

not possible to "drive the reaction to completion" within the ion source, so that the secondary ions can be gated into the drift space as, effectively, primary ions, good results can be obtained provided only that the gas pressure is high enough that the reaction has gone to effective completion before the swarm reaches the first of the three sampling positions used. In this instance the swarm profiles may appear quite distorted in comparison to a primary species, but the self consistency of results obtained simply by differencing the mean drift times leads us to believe that they are only slightly less accurate than for primary species.

Finally, the simple differencing procedure produces good drift velocity results even in some instances of a reversible reactions which does not "go to completion" at all, but approaches an equilibrium ratio of parent and daughter species abundances in the swarm. Provided that the parent and daughter species mobilities are sufficiently different, it is sometimes possible to distinguish the primary parent ions from the "tertiary" ions of the same species (formed by the breakup of secondary ions) by their positions in the profile, and to apply the mean drift time rule only to that part of the total profile that represents the true primaries. This technique has been used to extend the mobility measurements for certain primary ions such as N_2^+ well into ranges of E/N in which the secondary ion N_4^+ has become the predominant species in the swarm.[A5,C3]

2. Longitudinal Diffusion Coefficients for Primary Ions.

Following the addition of the Tyndall gate to the ion source, data began to be obtained, for primary ions, that did fit the mathematical model to an impressive degree. A figure we have presented in earlier reports[A3,5,C3] shows the histogram of an experimental profile and the smooth curve of the model, superimposed and normalized to each other at the peak; the two are in complete agreement within the counting statistics of the former far down onto the wings of the curve. Any reaction input of these ions derived from ions of a different

mobility would be clearly discernable as a bulge on the experimental histogram, even if the relative number of such reaction-produced ions represented only a small fraction of the total number of ions of that species. We have observed a number of such cases, and detailed shape comparisons have proved valuable in establishing the nature of the reaction pattern.

Space charge effects on the widths of the peaks are still observed unless the initial ion density is held much lower than we had supposed would be necessary, but with a suitable upper limit on this parameter, fitting of the model to the data results in apparent D_L values, at low E/N, that are in satisfactory agreement with the Einstein Equation values.[A3,5,C1] (For positive ions, the apparent D_L at low E/N has invariably been somewhat larger than the Einstein value, but it could generally be made to agree within about 10%. Oddly enough, for negative ions the reverse proved generally to be the case; the apparent D_L at low E/N was usually a little smaller than the Einstein value.) As E/N was increased above the low field range, D_L was shown to increase very rapidly (by at least one order of magnitude within our accessable range of E/N), and to become several times larger that the transverse coefficient D_T (see below). These results were the first direct measurements of D_L ever published[A3] for any ions in gases. The observed behavior of D_L was in general agreement with theoretical predictions of Wannier in a series of landmark papers, published almost twenty years previously, that still represent almost the sole attempt to deal theoretically with the high E/N case; his results have long formed the basis for most discussions of the ion energy distribution at high E/N. Our results represented the first experimental verification of important aspects of this theory. They verify that changes in the energy distribution are manifested most dramatically in the diffusion coefficients, especially in the longitudinal coefficient, and hence that diffusion coefficients may represent the most sensitive probe available for further study of the still largely unknown subject

of the energy distribution in high fields. (It may be noted that, to the extent that high field results can be correctly related to the energy distribution, they may be useful in predicting mobilities and diffusion coefficients at very high temperatures that are not readily accessable by more conventional means.)

3. Primary Ions: Transverse Diffusion Coefficients and the Rates of Depleting Reactions by the Attenuation Technique

It was further shown, using experimental data for K^+ ions as an example of a non-reacting primary ion, that the mathematical model for a primary ion swarm accounts very accurately for the attenuation or fall-off in overall intensity of the swarm profile with increasing drift distance, due to the diffusive spreading of the swarm transverse to the drift direction. A set of seven profiles calculated for a series of different drift distances, and containing only one common normalization constant, was shown to reproduce faithfully, with only one normalization, all seven of a corresponding set of experimental profiles.[A4,C3] In this instance, the data used were for low E/N, and the calculation utilized the value for the transverse diffusion coefficient, D_T, inferred from the experimental mobility through the Einstein Equation. The excellent agreement indicated that the fall-off or attenuation of the profile intensity with drift distance z should be usable for the measurement of D_T at higher values of E/N where it could not be simply inferred from the Einstein Equation.

In practice, it was shown to be sufficient to compare simply the fall-off with z of the integral of the experimental profiles with the time integral of the mathematical model, in order to determine D_T.[A2-4,C2,3] This fact permits both the data taking and the analysis to be greatly simplified, but also has the following very important consequence. The detailed profile computed for each value of z is of course dependent on the value assumed for D_L, as well as for D_T, but it was shown that the fall-off of the integral of the profile was quite insensitive to the assumed value of D_L. Similarly, in the detailed

fitting of individual profiles involved in evaluating D_L (see previous section), the results were equally insensitive to the value assumed for D_T in the calculation. (The value of D_T affects the normalization but not the shape of the computed profiles, while the value of D_L affects the width and shape of the profile but not its integral.) Thus the determinations of the two diffusion coefficients are effectively decoupled and made independent, to a good approximation.[A3,4,C3]

Like D_L, D_T was also shown in several cases to increase sharply with E/N above the low field region, but not as rapidly; at the highest E/N values accessable to us, it had increased about an order of magnitude above the low field value of the Einstein Equation, but was only about 1/3 as large as was D_L. This latter finding was in agreement with the predictions of Wannier, and our results were the first verification for ions of the predicted disparity between the two coefficients.

A most notable exception to the behavior described above was observed in the case of N_2^+ ions in N_2, the only case of an identical ion and molecule for which we have, thus far, obtained a satisfactory determination of D_T at high E/N;[A3,C3] in this instance D_T did not display the usual sharp increase, but remained essentially constant. It is believed that this behavior is probably associated with the presence of resonant charge exchange in this symmetrical ion-molecule case, and that the result may be general for such cases. The longitudinal coefficient for this case, while increasing sharply with E/N in the same general way as in other cases, did not increase by nearly as large a factor over the accessable range of E/N as did the other cases. Similar behavior was noted for O_2^+ and O_2^- in O_2.[B2,C4] These facts are indicative of a quite significantly different high E/N velocity distribution in the presence of resonant charge exchange.

The immediately preceding discussion has, for simplicity, been couched entirely in terms of a non-reacting primary ion species. The presence of a reaction which depletes the primary ion swarm during the drift period will obviously also contribute to the fall-off of the profile integral and thus interfere with the described evaluation of D_T. We have however found it possible in favorable cases to unscramble the reaction and transverse diffusion effects by utilizing the fact that reaction frequencies increase with increase of the gas density N (as N or N^2, according to whether the reaction is 2-body or 3-body, respectively), while the diffusion rate decreases, as 1/N. At low E/N, D_T may be assumed to have the value given by the Einstein Equation, so that the reaction rate can be obtained unambiguously from the attenuation data.[A2,C2] For higher E/N, a first approximation to D_T is first obtained from data taken at low gas pressures (small N), and correspondingly large drift distances, for which the reaction rate is small and is assumed to be given by the rate constant at low E/N. The resulting D_T values are then used with data taken at higher pressures (and correspondingly shorter drift distances), for which the reaction rate is large, to evaluate the reaction rate constant as a function of E/N. An iterative procedure may be followed, in the analysis of the two sets of data, to improve the initial approximations to D_T and the rate constant; a single iteration was however found to be sufficient in several cases.[A3-5,C3]

We have in this fashion succeeded in evaluating the rate constants, as functions of E/N over a considerable range, for several 3-body depleting reactions as listed in Sec. IV-A, with rather unprecedented uncertainties of as little as 10%. Necessary conditions for this attenuation technique to be useful are first, that the overall reaction pattern be simple enough that one can be certain that the primary ions are depleted by only the one reaction of interest. Secondly, if the reaction is reversible so that

"tertiary" ions of the original primary species are re-created in flight from secondary ions, either the rate of the reverse reaction must be very small compared to the forward reaction, or the mobility of the secondary ions must be sufficiently different from that of the primary ions that one can clearly distinguish the tertiary ions in the profile from the primary ions. These conditions could be shown to be met for the listed cases over some range of E/N, and in general it was the violation of these conditions at higher E/N that set the limits of the E/N range over which the reaction rate constants could be determined by this method. In the gases most recently studied, the inability to satisfy these conditions is responsible for the fact that only one of several interesting reactions (the O^- to O_3^- reaction) has been evaluated by this method.[B2,C4]

For these cases in which the necessary conditions can be met, the attenuation method offers the very important advantage that it is independent of mass discrimination effects in the relative efficiencies with which different ion species are sampled from the drift tube. Our unique feature of the movable ion source is obviously essential to the use of such a method. In addition, we have found that our wide range of available values of the drift distance, and the substantial number of different values of z available in that range, have been very important to the power and flexibility of the method.

4. Recent Developments: New Methods for Obtaining Reaction Rates in a Wider Variety of Cases

All of the analysis of the data discussed so far is based on the analytic expression for the space and time dependence of the density of a primary ion swarm, introduced into the drift region instantaneously at t = 0 as a finite diameter disc in the plane z = 0. We have also made substantial progress during the term of this grant on the more general problem of the analysis of

the profiles of product ions formed by reactions within the drift space.[B2,C4] A quite general expression has been written down from which one can in principle calculate the profiles of product ions of arbitrary order p (generated from the primary ions through a sequence of p-1 successive reactions), and this calculation has been carried out explicitly for secondary and tertiary ions. A quite exciting development has been made in the case of a reversible or "forward-backward" reaction, in which secondary ions may revert back to the primary species, i.e., form "tertiary" ions of the same species as the primaries. (These can, of course, then react again to form "quaternary" ions of the same species as the secondaries, and so on ad infinitum.) This is a situation of real practical interest which has been encountered repeatedly in the real cases we have studied. Because of the difficulty of distinguishing the "primary", "tertiary", etc., ions from one another, it is obvious that one could deal successfully with this case using separate expressions for secondary, tertiary, etc. profiles only under very restricted conditions; in particular, the pressure and drift distance would have to be such, in relation to the rates of both the forward and backward reactions, that only a negligible fraction of the ions would go through the reaction cycle more than once or twice during their transit. The rates of the two reactions will in general vary differently with E/N according to the energetics of the reaction, and study of the E/N dependence is a valuable means of exploring the energetics. A restriction to conditions under which few ions would go through repeated reaction cycles represents a fairly severe restriction on ones ability to exploit this situation.

The new development applies to a forward-backward reaction situation in which a given ion in the swarm may have gone through the reaction cycle an arbitrary number of times. The profile of the "parent" ion species is expressed as a sum of the profiles of all the odd order product spectra to

infinite order, and the "daughter" species as the sum of all the even orders. The summations have been carried out explicitly, giving a final result that is in closed form except for one final integration; a program has been written for the computer that carries out this integration numerically for any choice of the applicable parameters, i.e., the rates of the two reactions and of any additional depleting reactions of either species, and the mobilities and diffusion coefficients of both species.[C4]

Fitting of these multi-parameter calculations to experimental data will obviously not provide a sensitive evaluation of all of the parameters in arbitrary situations. Application of these results requires considerable exploration, by means both of analytic approximations and of test calculations and comparisons with real data, to find those situations in which the values of one or at most two of the parameters can be closely related to some distinctive feature of the calculated profiles. For the full forward-backward reaction expression, it can readily be shown that the profile shape will not be very sensitive to the reaction rates unless the mobilities of the parent and daughter species differ from each other substantially. The full expression has as yet not been fully explored because in the case of the $O_2^+ \leftrightarrow O_4^+$ reaction, the only reversible reaction which has been studied extensively since the development of this analytical result, the mobilities of the two species involved are very nearly equal. However, we believe that this analytical result will form the basis for many future developments.

Extensive explorations have been carried out for the less general situation in which there is no reverse reaction.[C4] An analysis of the secondary ion profile has been established, whose usefullness is again restricted to the case that the primary and secondary ion mobilities be markedly different. If it is the primary ion that has the larger mobility, the analysis predicts

a secondary ion profile whose leading edge is a sloping, nearly straight line on a semilog plot. Test calculations have been made to verify a simple relation between the slope of this line and the rate of the reaction which creates the secondary ions, and to determine the sensitivity of the slope to the assumed values of the other parameters. The analysis was used successfully to evaluate the rate of the reaction $O^- + 2O_2 \rightarrow O_3^- + O_2$ at low E/N, giving a result in satisfactory agreement with results, for the same reaction, by the primary ion attenuation technique.[B2,C4] The secondary ion profile analysis was also used to evaluate the rate, at higher E/N, of the reaction $O^- + O_2 \rightarrow O_2^- + O$, giving a result in very satisfactory agreement with those of other investigators elsewhere.[B2,C4] Like the primary ion attenuation technique, the secondary ion profile fit technique is unaffected by possible mass discrimination effects in the relative sampling efficiency for parent and daughter species.

We have also investigated an entirely different technique for the forward-backward reaction situation which is particularly applicable to cases where the mobilities of the parent and daughter species are nearly equal.[C4] It is easily shown that the ratio of the forward to backward reaction frequencies is determined if one can measure absolutely the equilibrium ratio of the total abundances of the two species integrated over the entire volume of a pulsed swarm. For this determination it is in fact unnecessary to pulse the source in our usual way; one can just as well run the source in a steady or dc mode, and measure simply the absolute ratio of the steady currents of both species over the entire cross section of the ion stream. (These are well known facts that have been utilized by many previous investigators.) Since our apparatus samples ions only on the drift tube axis, and thus we measure only a fraction of the total current that depends on the transverse

diffusive spread of the ion swarm or stream, our ratio can accurately represent the total current ratio only if the diffusive spreading is the same for both species. The diffusion coefficients in turn are related to the mobilities, at least at low E/N, and hence the limitation of this whole approach to the cases where the mobilities of the two species are nearly equal. In contrast to the previously discussed methods, our measured ratio will unfortunately be directly dependent on any mass discrimination effects. Such effects almost surely exist, are not known, and are probably not even very constant in time, so all results we have quoted that depend on this ratio evaluation have been described as qualitative, and assigned a large possible error.

As already stated, the equilibrium ratio will give only the ratio of the forward and backward reaction frequencies. We have however shown[C4] that the absolute magnitude of the reverse reaction frequency can be obtained by studying the change in the ratio with increasing drift distance, before equilibrium is reached - in particular, it is related rather simply, under certain restrictions, to the initial slope of the ratio, plotted against z, at small z. Thus in principle one can obtain, from the initial slope of the ratio at small z and the equilibrium ratio at large z, an evaluation of both the forward and backward reaction frequencies; here again, the movable ion source proves to be invaluable in extending the power of our methods. An independent check on the possibility of really serious errors, due to the mass discrimination, is available in some cases through a separate measurement of the forward reaction frequency by the primary ion attenuation technique.

This method has been utilized [B3,C4] to evaluate the forward and backward

rate constants for the two reversible reactions $O_2^+ + 2O_2 \rightleftarrows O_4^+ + O_2$ (See footnote*) and $NO^+ + 2NO \rightleftarrows NO^+ \cdot NO + NO$. The results showed a much larger scatter than those from our other methods, and they have been considered to be only qualitative.

D. Summary of Section IV

In this discussion of the research conducted during the tenure of the present grant, we have attempted to give a deliberately qualitative but comprehensive overview of the directions the research has taken during this period and the general nature and uniqueness of the results achieved. The intent was to show clearly the extent to which the goals that motivated the original concept of the drift tube mass spectrometer have been achieved and sometimes exceeded, to show the advances that have been made in both the types of results that can be obtained and in the accuracy of these results, and in the increased complexity of the reaction situations which can be handled. It is hoped that this discussion conveys some sense of the greatly increased power that has been brought to the area of ion swarm research.

As stated, the report has been deliberately qualitative; it is not intended to represent a complete technical discussion of all of the results for the expert in the field. Frequent use has been made of such phrases as "in favorable cases" or "under certain restrictions" without going into careful detail; for such details, which are frequently quite involved, the interested reader is referred to the detailed reports and articles listed in the Publications section.

In the same vein, we have made no attempt here to reference any of the large amount of related work of other laboratories, whether concurrent with

*The forward reaction shown here is of considerable aeronomic importance, as it is the first step in a chain of reactions producing water vapor ion clusters in the D region of the atmosphere (E.E. Ferguson and F. C. Fehsenfeld, Jour. of Geophysical Research 74, 5743 [1969]).

the present work or from an earlier era; indeed, the only reference in the text are to items in our own Publications list in Section V. These references are intended only to assist the reader in coordinating the general descriptions of the present report with the detailed discussions available in the other publications, and it is to them that the reader is directed for the detailed relationship to other work.

V. PUBLICATIONS AND REPORTS

A. Journal Articles (Published)

A1 "Mobilities of Mass-Identified H_3^+ and H^+ Ions in Hydrogen," by D. L. Albritton, T. M. Miller, D. W. Martin, and E. W. McDaniel, Phys. Rev. 171, 94-102 (1968).

A2 "Reactions of H^+ in H_2 and D^+ in D_2; Mobilities of Hydrogen and Alkali Ions in H_2 and D_2 Gases," by T. M. Miller, J. T. Moseley, D. W. Martin, and E. W. McDaniel, Phys. Rev. 173, 115-123 (1968).

A3 "Longitudinal and Transverse Diffusion Coefficients of Mass-Identified N^+ and N_2^+ Ions in Nitrogen," by J. T. Moseley, R. M. Snuggs, D. W. Martin, and E. W. McDaniel, Phys. Rev. Ltrs. 21, 873-875 (1968).

A4 "Measurement of Transport Properties of Ions in Gases; Results for K^+ Ions in N_2," by J. T. Moseley, I. R. Gatland, D. W. Martin, and E. W. McDaniel, Phys. Rev. 178, 234-239 (1969).

A5 "Mobilities, Diffusion Coefficients, and Reaction Rates of Mass-Identified Nitrogen Ions in Nitrogen," by J. T. Moseley, R. M. Snuggs, D. W. Martin, and E. W. McDaniel, Phys. Rev. 178, 240-248 (1969).

A6 "Possible Sources of Large Error in Determinations of Ion-Molecule Reaction Rates with Drift Tube-Mass Spectrometers," by E. W. McDaniel, J. Chem. Phys. 52, 3931-3935 (1970).

B. Journal Articles (To be submitted)

B1 "Mobilities and Longitudinal Diffusion Coefficients of Mass-Identified Potassium Ions and Positive and Negative Oxygen Ions in Oxygen," by R. M. Snuggs, D. J. Volz, J. H. Schummers, D. W. Martin, and E. W. McDaniel (to be submitted to Phys. Rev., 1970).

B2 "Ion Molecule Reactions between O^- and O_2 at Thermal Energies and Above," by R. M. Snuggs, D. J. Volz, I. R. Gatland, J. H. Schummers, D. W. Martin, and E. W. McDaniel (to be submitted to Phys. Rev., 1970).

B3 (tentative title) "Mobilities and Longitudinal Diffusion Coefficients of Mass-Identified Potassium Ions and Nitric Oxide Ions in NO Gas," by D. J. Volz, J. H. Schummers, R. D. Laser, D. W. Martin, and E. W. McDaniel (to be submitted to Phys. Rev., 1970).

C. Technical Reports

C1 "Measurement of the Low-Energy Transport Parameters of Mass-Identified Ions in Gases; Mobilities of H_3^+ and H^+ Ions in Hydrogen," by D. L. Albritton, D. W. Martin, E. W. McDaniel, T. M. Miller, and J. T. Moseley (May 10, 1967). (Adapted from the Ph.D. thesis of Daniel Lee Albritton.)

C2 "Measurement of the Low-Energy Transport Parameters of Mass-Identified Ions in Gases; Reactions of H^+ in H_2 and D^+ in D_2," by T. M. Miller, D. W. Martin, E. W. McDaniel, J. T. Moseley, and R. M. Snuggs (February, 1968). (Adapted from the Ph.D. thesis of Thomas Marshall Miller.)

C3 "Mobilities, Diffusion Coefficients, and Reaction Rates of Mass-Identified Nitrogen Ions in Nitrogen," by J. T. Moseley, D. W. Martin, E. W. McDaniel, R. M. Snuggs, and T. M. Miller (August 15, 1968). (Adapted from the Ph.D. thesis of John Travis Moseley.)

C4 "Mobilities, Longitudinal Diffusion Coefficients, and Reaction Rates of Mass-Identified Positive and Negative Oxygen Ions in Oxygen," by R. M. Snuggs, D. J. Volz, J. H. Schummers, R. D. Laser, I. R. Gatland, D. W. Martin, and E. W. McDaniel (March 29, 1970). (Adapted from the Ph.D. thesis of Robert Marvin Snuggs.)

D. Papers Presented at Meetings and Conferences (Orally presented by underlined author.)

D1 "Mobilities of H^+ and H_3^+ Ions in Hydrogen Gas," by D. L. Albritton, T. M. Miller, J. T. Moseley, D. W. Martin, and E. W. McDaniel, 19th Annual Gaseous Electronics Conference, Atlanta, Ga., October 1966.

D2 "Measurements of the Thermal Reaction Rate Coefficient for $H^+ + 2H_2 \rightarrow H_3^+ + H_2$," by T. M. Miller, J. T. Moseley, D. W. Martin, and E. W. McDaniel, Fifth International Conference on the Physics of Electronic and Atomic Collisions, Leningrad, USSR, July, 1967.

D3 "Mobilities of Mass-Identified H^+ and H_3^+ Ions in Hydrogen," by D. L. Albritton, T. M. Miller, J. T. Moseley, D. W. Martin, and E. W. McDaniel, Eighth International Conference on Phenomena in Ionized Gases, Vienna, Austria, August, 1967.

D4 "Mobilities and Longitudinal Diffusion Coefficients of Mass-Identified Nitrogen and Potassium Ions in Nitrogen," by J. T. Moseley, R. M. Snuggs, D. W. Martin, E. W. McDaniel, and T. M. Miller, 21st Annual Gaseous Electronics Conference, Boulder, Colorado, October, 1968.

D5 "Transverse Diffusion Coefficients and Ion-Molecule Reaction Rates of Mass Identified Nitrogen and Potassium Ions in Nitrogen," by E. W. McDaniel, D. W. Martin, R. M. Snuggs, and J. T. Moseley, 21st Annual Gaseous Electronics Conference, Boulder, Colorado, October, 1969.

D6 "Possible Sources of Large Error in Determinations of Reaction Rates with Drift Tube-Mass Spectrometers," by E. W. McDaniel, 22nd Annual Gaseous Electronics Conference, Gatlinburg, Tenn., October, 1969. (This was the lead-off talk of a panel discussion led by Dr. McDaniel.)

D7 "Mobilities and Longitudinal Diffusion Coefficients of Mass-Identified Oxygen and Potassium Ions in Oxygen," by R. M. Snuggs, D. J. Volz, J. H. Schummers, D. W. Martin, and E. W. McDaniel, 22nd Annual Gaseous Electronics Conference, Gatlinburg, Tenn., October, 1969.

E. Review Articles

E1 "Drift Tube Studies of the Transport Properties and Reactions of Slow Ions in Gases," by E. W. McDaniel, a chapter in the book "Case Studies in Atomic Collisions Physics," North-Holland Publ. Co., Amsterdam, 1969 (Pages 1-46).

E2 "Ion-Neutral Experiments," by E. W. McDaniel, in "Methods of Experimental Physics," Vol. 7-A, on Atomic Interactions, edited by B. Bederson and W. L. Fite, Academic Press, New York, 1968 (Pages 361-390).

F. Books

F1 "Case Studies in Atomic Collisions Physics," edited by E. W. McDaniel and M. R. C. McDowell, North-Holland Publ. Co., Amsterdam, 1969 (593 pages).

F2 "Ion-Molecule Reactions," by E. W. McDaniel, V. Cermak, A. Dalgarno, E. E. Ferguson, and L. Friedman, Wiley, New York, 1970 (370 pages).

F3 "The Mobility and Diffusion of Ions in Gases," by E. W. McDaniel and E. A. Mason, (a monograph in preparation, of approximately 350 pages).

G. Seminar Talks

E. W. McDaniel has presented seminar talks dealing with this research at the following institutions:

Oak Ridge National Laboratory
National Bureau of Standards, Boulder
Rice University
Physical Chemistry Laboratory, Czech Academy of Sciences, Prague
Newcastle University, England
U. K. Atomic Energy Research Establishment, Culham, England
Atomic Physics Research Institute, Amsterdam
University College, London, England
University of Belfast, Northern Ireland
Cambridge University, England
University of York, England
Queen Mary College, University of London
University of Sussex
University of Milan, Italy
University of Catania, Sicily
University of Freiburg, Germany
University of Missouri
University of Louisville
Gordon Conference
Yale University
Army Ballistic Research Laboratory, Aberdeen, Md.

VI. PERSONNEL

A. Faculty Members

Drs. Earl W. McDaniel and David W. Martin, both Professors in the School of Physics of the Georgia Institute of Technology, have collaborated in this research from the inception of the drift tube mass spectrometer program some 12 years ago. Both have received direct financial support for their participation from this grant.

B. Postdoctoral Fellow

Dr. Donald J. Volz has participated in this research since September, 1968. He has utilized equipment, supplies, and services supported by this grant, but has not received any direct salary support from the grant.

C. Graduate Students

Daniel Lee Albritton: Thesis entitled "The Mobilities of Mass-Identified H_3^+ and H^+ Ions in Hydrogen" submitted March, 1967; Ph.D. awarded in June, 1967. (Thesis Adapted as a Technical Report, Item C1, Publications section).

Thomas Marshall Miller: Thesis entitled "Reactions of H^+ in H_2 and D^+ in D_2 Gases" submitted February, 1968; Ph.D. awarded in June 1968. (Thesis adapted as a Technical Report, Item C2, Publications section).

John Travis Moseley: Thesis entitled "Mobilities, Diffusion Coefficients, and Reaction Rates of Mass-Identified Nitrogen Ions in Nitrogen" submitted August, 1968; Ph.D. awarded in June, 1969. (Thesis adapted as a Technical Report, Item C3, Publications section).

Robert Marvin Snuggs: Thesis entitled "Mobilities, Longitudinal Diffusion Coefficients, and Reaction Rates of Mass-Identified Positive and Negative Oxygen Ions in Oxygen" submitted March, 1970; Ph.D. awarded in June, 1970. (Thesis adapted as a Technical Report, Item C4, Publications section).

John H. Schummers: Has participated in this research since September, 1968. Admitted to Candidacy for the Ph.D., and currently engaged in thesis program.

Joel T. Kalb: Participated in this research for several months in 1968-9, but no longer associated with this program.

VII. RECOGNITIONS AND AWARDS

In recognition, in part, of the drift tube mass spectrometer research program supported by this grant (as well as other research activities at this institution in the general field of Atomic Collisions), the following national meetings have been or are scheduled to be held at the Georgia Institute of Technology:

19th Annual Gaseous Electronics Conference (a Topical Conference of the American Physical Society), Atlanta, October, 1966.

1971 Annual Meeting of the Division of Electron and Atomic Physics (DEAP) of the American Physical Society, Atlanta, scheduled for December, 1971.

Dr. E. W. McDaniel was awarded the following fellowships, which enabled him to spend some 14 months in independent study in Europe, in residence at the University of Durham, England, during 1966-7:

Fulbright-Hays Act Senior Research Scholarship, 1966-7.

Guggenheim Fellowship, 1966-7.

VIII. ACKNOWLEDGEMENT

During the period in which the drift tube mass spectrometer research program at the Georgia Institute of Technology has been partially supported by the present grant from the U. S. Air Force Office of Scientific Research, there has been additional partial support of the program from the Office of Naval Research in Project SQUID, under successive subcontracts with the University of Virginia and Purdue University.

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13 ABSTRACT

A previously developed Drift Tube Mass Spectrometer apparatus, for the study of the drift transport in weak fields of low density ion swarms in gases, has been applied to the quantitative measurement of drift velocities and mobilities, of longitudinal and transverse diffusion coefficients, and of the nature, order, and rate coefficients of ion-molecule reactions. Completed studies include, in the gases H_2, D_2, N_2, O_2, and NO, all of the positive (and for O_2 and NO also the negative) ion species found to be formed from the molecules of the gas by electron bombardment, or formed by reactions of such primary ions with the molecules of the gas. The mean ion energies, controlled by the ratio of the electric field strength E to the gas number density N, vary from essentially thermal energy (at room temperature) to as much as several electron-Volts, over the range of E/N of the measurements. A comprehensive though qualitative description is given of the very significant advances that have been made in the capabilities of ion swarm methods to yield new kinds of basic measurements and results of unprecedented accuracy.